



Selective catalytic reaction of NO_x with NH₃ over Ce–Fe/TiO₂-loaded wire-mesh honeycomb: Resistance to SO₂ poisoning



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ARTICLE INFO

Article history:

Received 8 November 2013

Received in revised form

24 December 2013

Accepted 4 January 2014

Available online 10 January 2014

Keywords:

SCR

Wire-mesh honeycomb catalyst

Surface sulfation

Resistance to SO₂

ABSTRACT

Ce–Fe/TiO₂/Al₂O₃/wire-mesh honeycomb catalyst (Ce–Fe/WMH) exhibited a high activity for the selective catalytic reduction (SCR) of NO_x in SO₂-containing gases. Analysis of fresh and spent catalysts by XRD, BET, XPS, TG and FTIR indicated that Ce sites were sulfated preferentially over Ce–Fe/WMH during the SCR reaction in the presence of SO₂, which could increase the amount of surface active oxygen species. On the other hand, the formation of surface hydroxyls due to the hydration of SO₄^{2–} could supply more Brønsted acid sites to adsorb NH₃ in the form of NH₄⁺. These two factors played significant roles in the good SO₂ durability of Ce–Fe/WMH. In addition, the sulfation of CeO₂ on catalyst surface might approach a stable state upon certain amount of SO₂ in reactant gas. The reaction mechanism study showed that only Eley–Rideal reaction pathway between ionic NH₄⁺, coordinated NH₃ and gaseous NO dominated in the reaction; the Langmuir–Hinshelwood reaction pathway was cut off by the sulfation, resulting in the rapid decrease of NO_x conversion in the early period of SCR reaction in the presence of SO₂.

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1. Introduction

Selective catalytic reduction (SCR) with ammonia is considered to be the most efficient and widely used technology for reducing NO_x emissions from stationary sources, such as power boilers and combustion furnaces. The commercial catalysts for this process are V₂O₅/TiO₂ (anatase) promoted by WO₃ or MoO₃, and they are preferentially applied in form of monolithic honeycombs due to their low pressure drop [1–3]. However, these vanadium-based catalysts are not environmental friendly as the vanadium is harmful to ecological environment. Therefore, an urgent demand for developing environmentally-benign deNO_x catalysts is put forward, and a lot of works have been performed to find new SCR catalyst systems, including zeolite [4,5] and transition metal oxides [6–8]. Recently, we also reported a Ce–Fe/TiO₂ catalyst [9], which was highly active in the SCR reaction within the temperature range of 160–350 °C.

Since typical coal fired exhaust contains variable amounts of SO₂ which can deactivate the SCR catalysts due to the formation of metal sulfate species [10] or the blockage of catalyst pore channels [11,12], understanding the effects of SO₂ on SCR activity is important for the development and application of appropriate catalysts.

Recently, some researchers reported that the catalysts would not be poisoned but significantly promoted by SO₂ [13–16]. All of these researchers agreed that the promoting role of SO₂ was resulted from the enhancement of NH₃ adsorption by the increase in surface acidity after sulfation. Upon sulfation of the catalyst, the acid sites increased in both number and strength. The latter was ascribed to the inductive effect of the S=O bond [17,18]. García-Bordejé et al. [19] also found that the sulfates formed could account for the improvement of the redox properties in the sulfated catalyst, which was beneficial for the reduction of NO with NH₃. However, most of researchers tested the SCR activity in SO₂-containing gases by changing the reaction temperature, which could not meet the demand of the practical application. The deactivation effect of SO₂ on SCR catalyst needs a long time to achieve steady state. It is thus necessary to investigate the influence of SO₂ on SCR activity in relatively long reaction time.

It is well known that the monolith catalyst is more representative in industrial application of NO reduction. Wire-mesh honeycomb is a new structured catalytic reactor, which combines the characteristics of wire mesh and monolith catalyst. In this work, a novel wire-mesh honeycomb-supported Ce–Fe/TiO₂ catalyst (Ce–Fe/WMH) was developed as a NH₃-SCR catalyst. The SO₂ durability (100 h) of the Ce–Fe/WMH at 250 °C was investigated, and then the nature of sulfated species and the mechanism of reaction were studied over the sulfated catalyst.

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2. Experimental

2.1. Catalyst preparation

Wire-mesh honeycomb (35 mm × 35 mm × 10 mm) was manufactured by stacking alternatively corrugated and plain wire mesh sheets, which contained 100 cells per square inch. As the bare surface of metal wire can hardly attach catalyst, the wire-mesh honeycomb substrate was coated with Al₂O₃ powder by an electrophoretic deposition (EPD) method as described elsewhere [20,21]. The alumina suspension was prepared with γ -alumina powders grinded from γ -alumina pellets. Polycyclic acid and aluminum isopropoxide were used as additives. The resulting Al₂O₃/wire-mesh honeycomb has a BET surface area of 87.5 m²/g measured by N₂ adsorption at 77 K.

Ce–Fe/TiO₂ was supported on the Al₂O₃/wire-mesh honeycomb by a two-step impregnation method. The detailed preparation procedure was described in our previous work [21]. This includes four steps: (i) impregnating the Al₂O₃/wire-mesh honeycomb in a TiO₂ slurry; (ii) drying at 100 °C; (iii) impregnating the TiO₂/Al₂O₃/wire-mesh honeycomb in an aqueous solution of cerium nitrate and iron nitrate; and (iv) drying at 100 °C and calcining at 500 °C. The resulting Ce–Fe/TiO₂/Al₂O₃/wire-mesh honeycomb catalyst was denoted as Ce–Fe/WMH, in which the Ce–Fe/TiO₂ loading of catalyst was about 130 g/l. The compositions of the Ce–Fe/TiO₂ as determined by atomic absorption spectrometer (AAS) with graphite furnace (AAnalyst 700, PerkinElmer) were about 1.4 wt% Fe, 24.1 wt% Ce and 74.5 wt% TiO₂, respectively, and the thickness of the Ce–Fe/TiO₂ washcoat was 30 μ m (as shown in Fig. S1).

2.2. Activity measurements

The catalytic studies were carried out in a square-shaped reactor (4.0 cm × 4.0 cm in width) made of stainless steel with a total bed length of 100 cm. The catalysts were placed inside the reactor in the middle. Free space between the catalyst and the reactor wall was filled with inert material to prevent bypass. The typical composition of the reactant gas was: 1000 ppm NO, 1000 ppm NH₃, 3% O₂, 100–1000 ppm SO₂ (when needed), and N₂ as the balance gas. The total flow rate was 2000 ml/min (refers to 1 atm and 298 K) which corresponded to gas hourly space velocity (GHSV) of 10,000 h^{−1}. The NO, NO₂ and O₂ concentrations were measured online by a flue gas analyzer (ecom-J2KN, rbr Messtechnik GmbH Inc.). The N₂O was analyzed by a gas chromatograph (Shimadzu GC–14C) with a Porapak Q column. The activities were evaluated in terms of NO_x conversion determined according to the following equation:

$$\text{NO}_x \text{ conversion} = \left(1 - \frac{[\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}}\right) \times 100\%$$

where [NO_x] = [NO] + [NO₂], and [NO_x]_{in} and [NO_x]_{out} were the concentrations of NO_x at the inlet and outlet of the reactor, respectively. In order to confirm that the decrease of NO_x was not caused by the adsorption of NO_x in the catalysts, at the beginning of each experiment, the catalyst was purged with the reactant gas until there was no difference between the inlet and the outlet gas.

2.3. Catalyst characterization

Scanning electron microscopy (SEM) of the catalyst was measured on a HITACHI S-4800 operating at 3.0 kV. The specific surface areas of the catalysts were measured by nitrogen adsorption using the Brunauer–Emmett–Teller (BET) method (Quadrasorb SI). Powder X-ray diffraction (XRD) measurements were carried out on a Rigaku D/MAX-2400 X-ray diffractometer with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) was implemented on a surface analysis system (Thermal ESCALAB 250) using Al K α radiation.

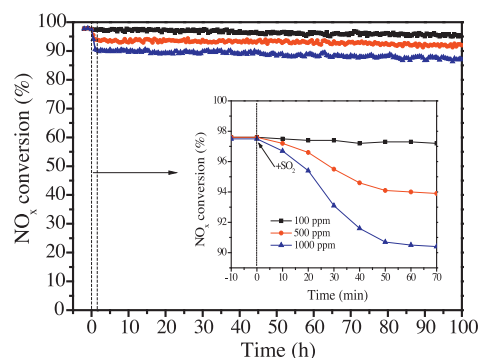


Fig. 1. Effect of SO₂ on NO_x conversion of Ce–Fe/WMH catalyst. Reaction conditions: [NO] = [NH₃] = 1000 ppm, [O₂] = 3 vol%, [SO₂] = 100, 500 and 1000 ppm (when used), N₂ balance and GHSV = 10,000 h^{−1}, T = 250 °C.

The C 1s line at 284.6 eV was considered as a reference for the binding energy calibration. Fourier transform infrared spectroscopy (FT-IR) was performed with Bruker Vector FTIR spectrometer used a DTGS detector. Before the analyses, about 2 mg of the sample was ground, mixed, and palletized with pure KBr by a weight ratio of 1:100. Thermo gravimetric analysis (TGA) was carried out in a static N₂ atmosphere, using a TG/DTA 6300 instrument. An amount of 6–9 mg of each sample was analyzed between 20 and 1000 °C at a rate of 10 °C/min.

The in situ DRIFTS experiments were performed on a Bruker Vector FTIR spectrometer with in situ diffuse reflectance pool and high sensitivity MCT detector cooled by liquid N₂. An approximately 12 mg sample was finely ground and pressed into a self-supported wafer. Mass flow controllers and a sample temperature controller were used to simulate the real reaction conditions. Prior to each experiment, the wafer was heated to 350 °C in N₂ (99.999%) for 1 h and then cooled down to the desired reaction temperature. The background spectrum was collected in flowing N₂ and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 500 ml/min total flow rate, 500 ppm NO, 500 ppm NH₃, 3% O₂ and N₂ balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm^{−1}.

3. Results and discussion

3.1. Effect of SO₂ on NO_x conversion

Effects of SO₂ (100–1000 ppm) on SCR activity of Ce–Fe/WMH at 250 °C is illustrated in Fig. 1. Under the employed reaction condition without SO₂, a steady-state NO_x conversion of 97.6% was obtained. In the presence of 100 ppm SO₂, there was almost no change of NO_x conversion over the catalyst in the tested 100 h. However, when 500 ppm SO₂ was added to the feed, NO_x conversion decreased from 97.6% to 93.9% in the early 50 min (inset of Fig. 1), and then it could maintained at about 92% for 100 h. In the case of 1000 ppm SO₂, an obvious decrease in NO_x conversion from 97.6% to 90.3% also occurred after 50 min and then the conversion slightly decreased to 88% after 100 h. These results demonstrated that the Ce–Fe/WMH exhibited good resistance to SO₂ poisoning in the tested 100 h. Interestingly, the NO_x conversion variation trends in the first 50 min and following reaction time were different. It was inferred that the obvious decrease after the addition of SO₂ (500, 1000 ppm) was ascribed to the competitive adsorption of NO and SO₂. Since SO₂ and H₂O are present in the exhausts, the durability of SO₂ and H₂O was also studied on Ce–Fe/WMH (as shown in Fig. S2). It could be seen that the NO_x conversion retained about 70% at least for 100 h in the presence of 1000 ppm SO₂ and 10% H₂O at

Table 1
Surface atomic concentrations and binding energies of fresh and spent Ce–Fe/WMH catalysts.

Catalyst	Surface atomic concentration (%)					Binding energy (eV)	
	Ce	Fe	Ti	O	S	Ce 3d _{5/2} (v)	Ce 3d _{3/2} (u)
Ce–Fe/WMH	3.53	2.55	24.76	69.16	–	883.1	904.9
Ce–Fe/WMH(100 ppm)	3.62	1.85	16.52	72.16	5.85	882.8	904.3
Ce–Fe/WMH(500 ppm)	3.37	1.77	16.06	71.09	7.71	882.5	904.5
Ce–Fe/WMH(1000 ppm)	3.19	1.70	15.64	71.83	7.64	882.7	904.6

250 °C. Therefore, the Ce–Fe/WMH showed promising resistance to water vapor and SO₂ poisoning.

3.2. Characterization of fresh and spent catalysts

The X-ray diffraction patterns of the fresh Ce–Fe/WMH, Ce–Fe/WMH (100 ppm), Ce–Fe/WMH (500 ppm) and Ce–Fe/WMH (1000 ppm) catalysts are shown in Fig. 2, here the Ce–Fe/WMH (x ppm) refers to a spent catalyst tested in a reactant gas containing x ppm SO₂. Fresh Ce–Fe/WMH provided typical diffraction patterns for the cubic CeO₂ structure (PDF no. 34-0394), TiO₂ anatase phase (PDF no. 21-1272) and a little rutile phase (PDF no. 21-1276). For all the spent catalysts, no obvious change was observed in the lattice parameters of anatase and rutile, but the intensity of the diffraction peaks of cubic CeO₂ was slightly decreased, suggesting a loss of CeO₂ crystallinity after reactions in SO₂-containing gases. Moreover, no extra peaks ascribed to sulfated phase were observed in the XRD patterns, which indicated that the sulfated species might exist as either surface sulfate or amorphous bulk sulfate.

In order to identify the state of surface species after SCR reaction in the presence of SO₂, the catalysts were examined by XPS spectroscopy. The surface atomic concentrations of Ce, Fe, Ti, O and S, together with the binding energies of Ce 3d_{5/2} (v) and Ce 3d_{3/2} (u), are summarized in Table 1. In comparison with the fresh Ce–Fe/WMH, the spent catalysts showed a decrease in the surface concentrations of Ce, Fe and Ti.

Fig. 3(A) reveals the S 2p spectra of fresh and spent Ce–Fe/WMH catalysts. On the fresh Ce–Fe/WMH, no obvious S 2p band was observed, while an evident band attributed to S 2p was observed on all the spent catalysts. The binding energy of this S 2p band was 169.2 eV, which was consistent with the S (VI) oxidation state and assigned to the inorganic sulfate with ionic S–O bands [22,23]. Furthermore, the sulfur contents for Ce–Fe/WMH (100 ppm), Ce–Fe/WMH (500 ppm) and Ce–Fe/WMH (1000 ppm) were 5.85%, 7.71% and 7.64%, respectively (as shown in Table 1), revealing that the relative amount of sulfate did not increase with the concentration of SO₂ in reactant gas from 500 to 1000 ppm.

From the XPS results of Ce 3d in Fig. 3(B), two multiplets (u and v) could be found after fitting. The bands labeled u1 and v1 represent

the 3d¹⁰4f¹ initial electronic state, corresponding to Ce³⁺, whereas the peaks labeled u, u2, u3, v, v2, and v3 represent the 3d¹⁰4f⁰ state of Ce⁴⁺ ions [24,25]. The Ce³⁺ ratio, calculated by Ce³⁺/(Ce⁴⁺ + Ce³⁺), was increased as a result of Ce–Fe/WMH exposure to SO₂. Waqif et al. [26] reported that the SO₂ could act as a reducing agent, inducing a reduction from Ce⁴⁺ to Ce³⁺ on sample surface. All the spent Ce–Fe/WMH catalysts showed a little higher binding energies in Ce⁴⁺ characteristic peaks than fresh catalyst (as shown in Table 1), indicating an expansion of CeO₂ fluorite lattice. Again, this was caused by the increase of Ce³⁺, whose effective ionic radius is about 14% larger than that of Ce⁴⁺ in the same coordination [27]. According to the Yang et al. [28], the sulfation of CeO₂ could enhance the percent of Ce³⁺ on catalyst surface, resulting in the formation of

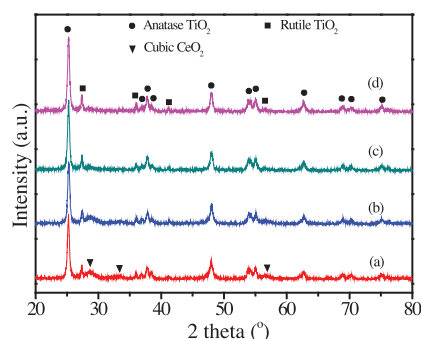


Fig. 2. XRD patterns of fresh and spent Ce–Fe/WMH catalysts. (a) fresh Ce–Fe/WMH, (b) Ce–Fe/WMH (100 ppm), (c) Ce–Fe/WMH (500 ppm), (d) Ce–Fe/WMH (1000 ppm).

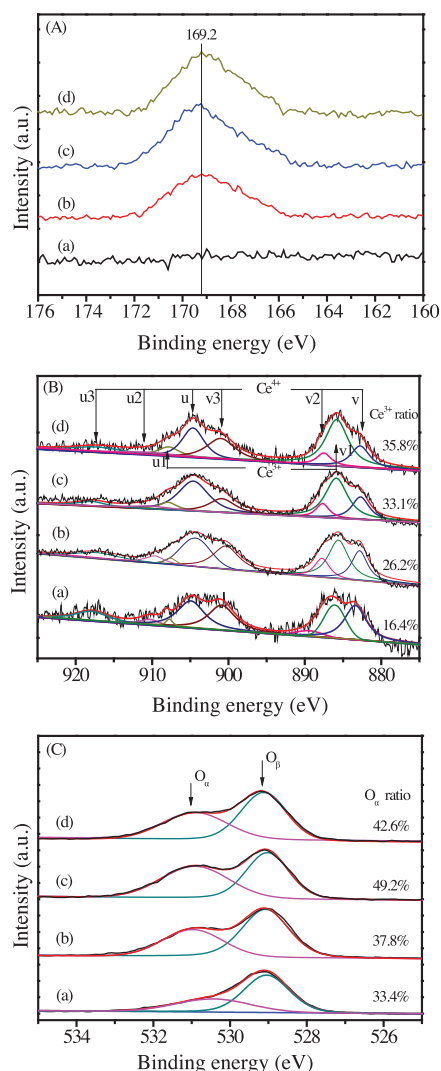


Fig. 3. XPS spectra of (A) S 2p, (B) Ce 3d and (C) O 1s of fresh and spent catalysts. (a) fresh Ce–Fe/WMH, (b) Ce–Fe/WMH (100 ppm), (c) Ce–Fe/WMH (500 ppm), (d) Ce–Fe/WMH (1000 ppm).

$\text{Ce}_2(\text{SO}_4)_3$. Thus, it was thought that $\text{Ce}_2(\text{SO}_4)_3$ was formed during the tested 100 h.

Fig. 3(C) revealed the fitted O 1s peaks for lattice oxygen O^{2-} at 529.0–529.3 eV (hereafter denoted as O_β) and chemisorbed oxygen at 530.7–531.1 eV (hereafter denoted as O_α), such as O_2^{2-} and O^- belonging to defect-oxide or hydroxyl-like group [29]. All the spent Ce-Fe/WMH catalysts showed an increase of the ratio of $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ compared to fresh catalyst, suggesting the presence of more defect-oxide or hydroxyl-like group on the catalyst surface. It could be inferred that these surface hydroxyls were mainly acidic due to the hydration of SO_4^{2-} to form S–OH group, supplying more Brønsted acid sites to adsorb NH_3 in the form of NH_4^+ in the SCR reaction. This hypothesis would be verified by the following in situ DRIFTS experiments. In addition, the Fe 2p and Ti 2p XPS spectra were also recorded (as shown in Fig. S3). The binding energies of Fe $2p_{3/2}$ (710.8 eV) and Fe $2p_{1/2}$ (724.5 eV) corresponded well with the Fe^{3+} species, and the binding energies of Ti $2p_{3/2}$ (458.6 eV) and Ti $2p_{1/2}$ (464.5 eV) were typical characteristics of Ti^{4+} [30]. Comparing to the spectra of fresh Ce-Fe/WMH, the spectrum intensities of Fe 2p and Ti 2p became weak for the spent catalysts, suggesting a decrease of the Fe and Ti surface atomic concentration. Nonetheless, the binding energies of Fe 2p and Ti 2p remained unchanged before and after SO_2 durability. It demonstrated that the iron or titanium species on catalyst surface was not sulfated during the tested 100 h, while the ceria was sulfated due to its higher binding energies in Ce^{4+} characteristic peaks after the reaction under SO_2 environment. This could also be supported by the surface atomic concentrations of Ce, Fe and Ti (as shown in Table 1). After the tested 100 h, the decrease of surface Ce concentration was much lower than those of Fe and Ti, which suggested that the sulfation mainly occurred on ceria sites during the reaction.

The above-mentioned XPS results indicated that SO_2 preferentially adsorbed on Ce sites during the tested 100 h, which could create more Ce^{3+} species on spent catalysts than those on fresh one. This would provide more oxygen vacancies on the catalyst surface and thus facilitate the activation and transportation of active oxygen species in reaction, which was beneficial to the SCR reaction.

TGA spectra of the fresh Ce-Fe/WMH, Ce-Fe/WMH (100 ppm), Ce-Fe/WMH (500 ppm), Ce-Fe/WMH (1000 ppm) and ammonium sulfate impregnated Ce-Fe/WMH catalysts are presented in Fig. 4. In the case of the fresh Ce-Fe/WMH, there was only one weight loss at 50–160 °C, which corresponded to H_2O desorption on the catalyst surface [31]. For spent catalysts, apart from the weight loss due to H_2O desorption, two new weight losses in the higher temperature range were also observed. The first small weight loss at 300–450 °C could be attributed to the decomposition of ammonium sulfate, and the second large weight loss at 670–800 °C was ascribed to the decomposition of metal sulfate (here $\text{Ce}_2(\text{SO}_4)_3$) [11,31]. These results suggested that the reaction between oxidized SO_2 and metal oxides predominated over the Ce-Fe/WMH in

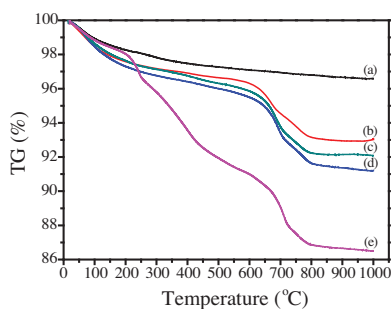


Fig. 4. TGA spectra of fresh and spent Ce-Fe/WMH catalysts. (a) Fresh Ce-Fe/WMH, (b) Ce-Fe/WMH (100 ppm), (c) Ce-Fe/WMH (500 ppm), (d) Ce-Fe/WMH (1000 ppm), (e) fresh Ce-Fe/WMH-containing ammonium sulfate.

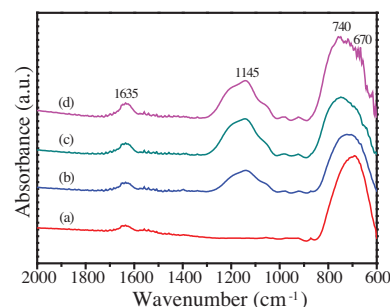


Fig. 5. FT-IR spectra of fresh and spent Ce-Fe/WMH catalysts. (a) fresh Ce-Fe/WMH, (b) Ce-Fe/WMH (100 ppm), (c) Ce-Fe/WMH (500 ppm), (d) Ce-Fe/WMH (1000 ppm).

the tested 100 h. In some literatures [11,31,32], the weight loss at relatively high temperatures due to the decomposition of metallic sulfates was thought to come from the decomposition of deposited ammonium sulfate during the heating course of the thermogravimetric analysis. Therefore, the impregnated ammonium sulfate on fresh Ce-Fe/WMH was also tested using TG to clarify how the sulfated CeO_2 was formed on catalyst surface. The resulting TG curve exhibited three types of weight losses at similar temperature range to those of the spent catalysts. However, the intensity of weight loss due to the decomposition of ammonium sulfate was much higher than that of the spent catalysts, and the intensity of weight loss due to sulfated Ce was lower. This implied that the sulfated CeO_2 was definitely formed by the reaction between oxidized SO_2 and cerium oxides during the SCR reaction.

FT-IR spectra of the fresh and spent catalysts are showed in Fig. 5. All catalysts exhibited vibration absorptions at wave numbers of 1635, 740 and 670 cm^{-1} , which could be attributed to different metal oxides [11]. Compared with the fresh Ce-Fe/WMH, the spent catalysts had a new adsorption at 1145 cm^{-1} , indicating the existence of SO_4^{2-} . Free SO_4^{2-} ion shows usually two infrared-active peaks at 1140 and 626 cm^{-1} [33], but the adsorption at 626 cm^{-1} was overlapped by the absorptions of metal oxides. These results demonstrated that sulfate species should be formed during the SCR reaction in the presence of SO_2 . Moreover, the IR adsorption intensity at 1145 cm^{-1} exhibited little difference between Ce-Fe/WMH (500 ppm) and Ce-Fe/WMH (1000 ppm) but this adsorption was obviously larger than that for Ce-Fe/WMH (100 ppm). This suggested that the amount of SO_4^{2-} species slightly increased within the tested SO_2 concentration (<1000 ppm). In addition, the band ascribed to the NH_4^+ species was not detected, indicating the sulfur ammonium presented in a scarce amount beyond IR detection limits.

The specific surface areas of the fresh and spent catalysts are listed in Table 2. It showed clearly that the surface areas of all the spent Ce-Fe/WMH decreased after reactions in the presence of SO_2 , which could be caused by formation/deposition of sulfated species on catalyst surface [13,34]. Yang et al. [28] reported that the surface area of $\text{Ce}_2(\text{SO}_4)_3$ was lower than that of CeO_2 . Combined with above results, the decrease of surface area of all the spent Ce-Fe/WMH was attributed to the formation of $\text{Ce}_2(\text{SO}_4)_3$ during the tested 100 h. Furthermore, there was little difference

Table 2
Specific surface areas of fresh and spent Ce-Fe/WMH catalysts.

Catalysts	BET surface area (m^2/g)
Fresh Ce-Fe/WMH catalyst	51.6
Ce-Fe/WMH catalyst (100 ppm)	41.1
Ce-Fe/WMH catalyst (500 ppm)	36.8
Ce-Fe/WMH catalyst (1000 ppm)	37.4

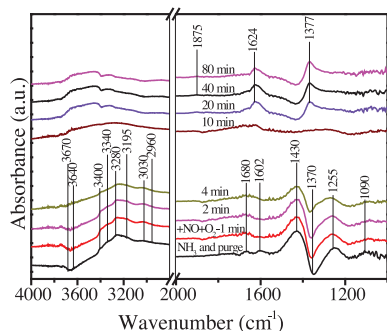


Fig. 6. In situ DRIFTS of reaction between $\text{NO} + \text{O}_2$ and pre-adsorbed NH_3 species at 250°C over Ce-Fe/WMH-S.

in surface area between Ce-Fe/WMH (500 ppm) and Ce-Fe/WMH (1000 ppm). It complied with the preceding demonstration that the formation of sulfated CeO_2 on catalyst surface might approach a stable state upon certain amount of SO_2 in reactant gas. It was noteworthy that the NO_x conversion variation trends in the first 50 min and following reaction time were different, both of which might be controlled by different mechanisms. The detailed SCR reaction mechanism over Ce-Fe/WMH-sulfation would be further investigated using in situ DRIFTS method in the following section.

3.3. Reaction mechanism over Ce-Fe/WMH-sulfation

In mechanism study, the fresh Ce-Fe/WMH was first pre-treated in a flow of 1000 ppm $\text{SO}_2 + 3\% \text{O}_2$ for 100 h, and then applied to DRIFTS analysis. The resulting sample was denoted as Ce-Fe/WMH-S. Fig. 6 shows the in situ DRIFTS spectra of the reaction between $\text{NO} + \text{O}_2$ and pre-adsorbed NH_3 species on Ce-Fe/WMH-S at 250°C . After NH_3 adsorption and N_2 purge at 250°C , the catalyst surface was mainly covered by ionic NH_4^+ (δ_s at 1680 cm^{-1} and δ_{as} at 1430 cm^{-1}) bound to Brønsted acid sites and coordinated NH_3 (δ_s at 1255 cm^{-1} and δ_{as} at 1602 cm^{-1}) bound to Lewis acid sites [35,36]. At the same time, N-H stretching vibration modes from ionic NH_4^+ ($3280, 3030$ and 2960 cm^{-1}) [37] and coordinated NH_3 ($3400, 3340$ and 3195 cm^{-1}) [38] also appeared, together with the negative bands at 3670 and 3640 cm^{-1} due to the hydroxyl consumption through interaction with NH_3 to form NH_4^+ . The intense negative band at 1370 cm^{-1} ($\nu_{as\text{S=O}}$) was caused by the interaction between sulfate species and NH_3 , in which ammonium sulfate might form on the catalyst surface. The band at 1090 cm^{-1} might be attributed to the perturbation of sulfate species ($\nu_{s\text{S-O}}$) through reaction with NH_3 to form ammonium sulfate [39]. After the introduction of $\text{NO} + \text{O}_2$, the bands ascribed to ionic NH_4^+ and coordinated NH_3 showed an obvious decrease in intensity and totally disappeared after 10 min, implying that the adsorbed NH_3 species could react with $\text{NO} + \text{O}_2$. Meanwhile, the negative band at 1370 cm^{-1} was recovered, suggesting that the NH_4^+ bound to sulfate species could also take part in the SCR reaction. This could explain the reason for the low ammonium sulfate deposition on catalyst surface during the SCR reaction in the presence of SO_2 . With the reaction time continuous increase, two new bands at 1377 and 1624 cm^{-1} appeared. They were assigned to the deposited sulfate species ($\nu_{as\text{S=O}}$) and adsorbed H_2O produced in the SCR reaction [40], respectively. These results suggested that $\text{NO} + \text{O}_2$ readily reacted with the adsorbed NH_3 species on Ce-Fe/WMH-S. After the pre-adsorbed NH_3 species were consumed, a new band at 1875 cm^{-1} attributed to gaseous NO [41] showed up.

Afterwards, the in situ DRIFTS measurement of reaction between NH_3 and pre-adsorbed NO_x species over Ce-Fe/WMH-S was carried out and the results are shown in Fig. 7. After $\text{NO} + \text{O}_2$ adsorption and N_2 purge at 250°C , two slight bands assigned to NO_2

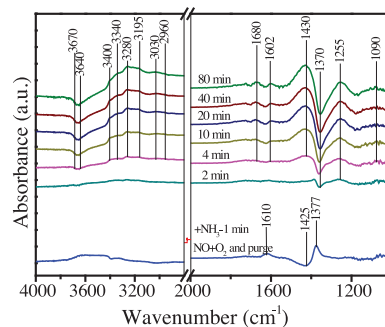


Fig. 7. In situ DRIFTS of reaction between NH_3 and pre-adsorbed NO_x species at 250°C over Ce-Fe/WMH-S.

(1610 cm^{-1}) and deposited sulfate species ($\nu_{as\text{S=O}}$) (1377 cm^{-1}) appeared [41,42]. The negative band at 1425 cm^{-1} could be assigned to the displacement of the sulfate species, implying that NO and SO_2 were adsorbed competitively on catalyst surface. The subsequent introduction of NH_3 resulted in the accumulation of adsorbed NH_3 species on catalyst surface, including ionic NH_4^+ (δ_s at 1680 cm^{-1} and δ_{as} at 1430 cm^{-1}) and coordinated NH_3 (δ_s at 1255 cm^{-1} and δ_{as} at 1602 cm^{-1}), similar to the results shown in Fig. 6. During the whole process, the band at 1624 cm^{-1} corresponding to adsorbed H_2O could hardly be detected. It indicated that the reaction between NH_3 and adsorbed NO_x species on Ce-Fe/WMH-S might be neglected.

Finally, the in situ DRIFTS measurement of SCR reaction over Ce-Fe/WMH-S as a function of time was conducted and the results are shown in Fig. 8. During the whole reaction process, only adsorbed NH_3 species were detected on catalyst surface, except for a weak band at 1875 cm^{-1} due to gaseous NO . This result showed that the reaction between adsorbed NH_3 and gaseous NO occurred on the Ce-Fe/WMH-S.

According to the above in situ DRIFTS results, it could be observed that most active sites were covered by adsorbed NH_3 species during the whole reaction process, and Brønsted acid sites and Lewis acid sites served as important active sites. In this way, NH_3 -SCR reaction of Ce-Fe/WMH-S might take place via an Eley-Rideal (E-R) type mechanism, where ionic NH_4^+ and coordinated NH_3 reacted with gaseous NO . During this process, the dehydrogenation of ionic NH_4^+ and coordinated NH_3 to NH_2 intermediate species by active oxygen species might be the rate determining step, followed by subsequent reaction with NO to produce H_2O and N_2 . In addition, the DRIFTS spectra of NH_3 adsorption on Ce-Fe/WMH-S and fresh Ce-Fe/WMH at 250°C were also recorded (as shown in Fig. S4(A)). It revealed that the amount of ionic NH_4^+ increased greatly after sulfation, which was in accordance with the above assumption that the Brønsted acidity was enhanced after sulfation (as shown in XPS results), but

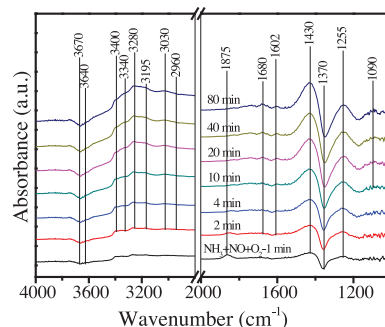


Fig. 8. In situ DRIFTS of reaction in $\text{NO} + \text{O}_2 + \text{NH}_3$ at 250°C over Ce-Fe/WMH-S.

the coordinated NH_3 was little influenced by SO_2 . The enhanced Brønsted acidity was mainly resulted from SO_4^{2-} on catalyst surface. Above all, the enhancement of Brønsted acidity and the increase of active oxygen species on catalyst surface caused by sulfation might be the important reason for the good SCR performance in SO_2 -containing gas over Ce–Fe/WMH.

Some researchers [43,44] reported that both the E–R mechanism (i.e. reaction of activated NH_3 species with gaseous NO) and the Langmuir–Hinshelwood (L–H) mechanism (i.e. reaction of adsorbed NO_x species with adsorbed NH_3 species) might happen during the SCR reaction over catalysts. In this work, the NO_x adsorption capability of Ce–Fe/WMH–S was much weaker than that of fresh Ce–Fe/WMH (as shown in Fig. S4(B)), and the reaction between adsorbed NO_x and NH_3 species on Ce–Fe/WMH–S was neglected (as shown in Fig. 7). Thus, it suggested that the L–H reaction pathway was cut off due to the sulfation process, which might result in the rapid decrease of NO_x conversion in the early period of SCR reaction in the presence of SO_2 (as shown in Fig. 1).

4. Conclusions

The SO_2 durability of the Ce–Fe/WMH was greatly improved by surface sulfation. From various characterizations, it was observed that sulfation could result in an enrichment of Ce^{3+} on catalyst surface and induced much Brønsted acid sites, both of which were conducive to SCR activity. Accordingly, the mechanism study showed that only the E–R reaction pathway dominated in the NH_3 –SCR reaction over sulfated Ce–Fe/WMH, which was an important reason for its enhanced SO_2 durability at 250 °C. For practical use, this Ce–Fe/WMH catalyst can be used for de NO_x process in the presence of SO_2 .

Acknowledgments

This work was supported by the National Basic Research Program of China (973 Program) (No. 2011CB936002) and National Innovation Experiment Program for University Students.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.01.008>.

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